PURDUE UNIVERSITY

SCHOOL OF CHEMICAL ENGINEERING
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May 13, 1996

Dr. Ken Wynne
Chemistry Division
Office of Naval Research
Ballston Commons Tower One
800 North Quincy Street
Arlington, Virginia 22217-5660

Dear Dr. Wynne:

Enclosed you will find a copy of my final report for Grant No. N00014-92-J-1415 entitled **Structure Property Relationships and Polymer Physics in High Temperature Polymers for Second Order Nonlinear Optics**. I have also enclosed information for the AASERT Grant No. N00014-93-1-0903.

The structural relaxation studies show strong promise, and we have preliminary results indicating that we will be able to PREDICT the temporal stability of chromophore orientation in polymer hosts. Enhanced temporal stability achieved in some systems, a deeper understanding of the physics influencing polymer relaxations, and a variety of novel materials have been tested tested. Even more new materials look promising, and many industrial and academic researchers have agreed to help synthesize some of the more complicated, novel materials. In addition, we are examining materials for other Navy researchers and grantees including Jim McGrath at Virginia Polytechnic Institute, and Michael Wright at Utah State. We are performing NMR experiments with Dr. Larry Merwin at China Lake in order to determine the onset of different types of mobility in these NLO systems. This is discussed in more detail below. I greatly appreciate your help in finding chemists who are interested in interacting with us, since the collaborations have been very helpful.

Please let me know if further information would be useful. Thank you very much for this opportunity and for all of your help.

Sincerely yours,

Hilary Lackritz
Assistant Professor
of Chemical Engineering

OFFICE OF NAVAL RESEARCH

END OF YEAR REPORT
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORT

for

GRANT: N00014-92-J-1415

R&T Code: 400x099yip01

Structure Property Relationships and Polymer Physics in High Temperature Polymers for Second Order Nonlinear Optics

Principal Investigator: Hilary S. Lackritz
Assistant Professor
School of Chemical Engineering
Purdue University
West Lafayette, Indiana 47907-1283

May 12, 1996

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OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT

a.   Number of papers submitted to refereed journals, but not published: 4

1.   Fu, C.Y.S.; Lackritz, H.S.; Priddy, D. B. Jr.; McGrath, J.E. "Effects of Chromophore Functionalization and Physical Aging during Poling on Chromophore Orientational Dynamics in Polyarylene Ethers for Second Order Nonlinear Optics" *Macromolecules*, in press.

2.   Ghebremichael, F.; Kuzyk, M.; Lackritz, H.S. ""Nonlinear Optics and Polymer Physics" *Progress in Polymer Science* , submitted 3/96. INVITED REVIEW ARTICLE (28 figures and 263 references).

3.   Ghebremichael, F.; Lackritz, H.S. "Linear Electro-optic Effects of Dye-Doped Polymers: Temperature and Poling Field Dependencies" *Journ. Opt. Soc. Am. B*, submitted 4/96.

4.   Medvedev, G.; Caruthers, J. M.; Lackritz, H.S. "Effect of Structural Relaxation and Physical Aging on the SHG Intensity Decay in Dye Polymer Systems for Nonlinear Optics" *Macromolecules*, submitted 5/96.

b.   * Number of papers published in refereed journals or refereed proceedings: 9

1.   Lackritz, H.S.; Liu, L.-Y.;Wright, M.E.; Mullick, S. "Study of Poling and Relaxation in Kink and Linear Main-Chain Functionalized Polymers for Second Order Nonlinear Optical Applications" *Macromolecules*, 1995, *28*, 1912.

2.   Pasmore, T.; Talbot, J.; Lackritz, H. S. "Monte-Carlo Simulations of Electric Field Hopping in Doped Polymer Thin Films" *Mol. Cryst. Liq. Cryst. Sci. Tech. B: Nonlinear Optics*, 1995, *10*, 295.

3.   Liu, L.Y.; Lackritz, H.S. "The Effects of Electric Field and Polymer Relaxation on the Rotational Brownian Motion of Chromophores in Polymer Films for Second Order Nonlinear Optics" *Mol. Cryst. Liq. Cryst. Sci. Tech. B: Nonlinear Optics*, 1995.

4.   Zhuang, X.; Lackritz, H.S.; Shen, Y.R. "Photo-isomerization of Polymer Monolayers and Multilayers on Water" *Chem. Phys. Lett.*, 1995, *246*, 279-284.

5.   Fu, C.Y.S.; Lackritz, H.S.; Priddy, D. B. Jr.; McGrath, J.E. "Polymer Physics and Structure/Property Relationships of Thermally Stable Polyarylene Ethers for

6. Wright, M. E.; Toplikar, E. G.; Lackritz, H. S.; Subramanyan, S. "A Preliminary Study of Poly(p-phenylene) Based NLO Materials" *Chem. Mater.*, in press.

7. Pasmore, T.A.; Talbot, J.; Lackritz, H.S. "Charge Transport through Polymer Thin Films for Second Order Nonlinear Optics" IEEE Conference on Electrical Insulation and Dielectric Phenomena Annual Report (Proceedings), **1995, 95CH35842, 646-649.**

8. Sullivan, L. A.; *Lackritz, H. S. "Dynamic Mechanical Analysis and Dielectric Relaxation for Second Order Nonlinear Optical Applications" *Materials Research Society Symposium Series,* **1995,** *392,* 69-75.

9. Chen, F.; Subramanyan, S.; *Lackritz, H.S. "Photopolymerization Dynamics of Acrolein onto Metal Substrates Using Surface Second Harmonic Generation" *Materials Research Society Symposium Series,* **1995,** *385,* 3-9.

c. Number of books or chapters submitted, but not yet published: <u>1</u>

1. Fu, C.S.Y.; Ostrowski, M.H.; *Lackritz, H.S. "Dielectric Relaxation Studies of Polymeric Nonlinear Optical Materials" in Dielectric Spectroscopy of Polymeric Materials, Runt, J. P. and Fitzgerald, J. J., Eds. ACS Symposium Series, American Chemical Society, Washington, D.C., accepted for publication. (*Invited Publication*)

d. * Number of books or chapters published: <u>0</u>

e. * Number of printed technical reports/non-refereed papers: <u>1</u>

1. Lackritz, H. S.; Ostrowski, M. H. "Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications" *Soc. Plastics Eng. Antec Proc.*, May **1996.**

f. Number of patents filed: <u>0</u>
g. * Number of patents granted: <u>0</u>
h. * Number of invited presentations: <u>14</u>

1. Sullivan, L.; *Lackritz, H. S. "Characteristic Relaxation Times in Polymers Studied by Nonlinear Optics, Dielectric Relaxation, and Dynamic Mechanical Analysis" presented at Wright-Patterson Air Force Base in Dayton, OH, April, 1995.

2. Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optics" presented at the Massachusetts Institute of Technology, Polymer Seminar Series, Cambridge, MA, May 1995.

3. Lackritz, H. S. "Polymer Physics Studied Using Second Order Nonlinear Optical Applications" presented at Hercules, Incorporated, Wilmington, DE, June 1995.

4. Lackritz, H. S. "Polymer Physics and Second Order Nonlinear Optical Properties of Polymeric Systems" presented at DuPont Corporate Research Laboratories, Wilmington, DE, June 1995.

5. Lackritz, H. S. "Design and Development of Polymers for Second Order Nonlinear Optics" presented at Kyoto Institute of Technology, Kyoto, Japan, July 1995 (Invited Lectureship).

6. Liu, L. Y.; *Lackritz, H. S. "Polymer Relaxations and Electric Field Effects in Polymers for Second Order Nonlinear Optics" presented at the International Conference on Organic Nonlinear Optics in Gunma, Japan, July 1995.

7. *Lackritz, H. S.; Sullivan, L. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optics" presented at the International Conference on Advanced Materials, International Union of Materials Research Societies, Cancun, Mexico, August 1995.

8. Lackritz, H. S. "Second Order Nonlinear Optical Polymer Dynamics" presented at Miami University, Materials Science Program, Cincinnati, OH, September, 1995.

9. Lackritz, H. S. "The Characterization of Polymer Dynamics in Poled Second Order Nonlinear Optical Polymers" presented at the Pacific Polymer Conference, Kauai, HI, December 1995.

10. Lackritz, H. S. "The Characterization of Polymer Dynamics in Poled Second Order Nonlinear Optical Polymers" presented at Princeton University, Department of Chemical Engineering, Princeton, NJ, January 1996.

11. Lackritz, H. S. "Polymer Physics and Electric Field Effects in Poled Polymers for Second Order Nonlinear Optics" presented at Notre Dame University, Department of Chemical Engineering, South Bend, IN, January 1996.

12. Lackritz, H. S. "Optical Characterization of Polymer Dynamics" presented at Northwestern University, Department of Chemical Engineering, Evanston, IL, February 1996.

13. *Lackritz, H. S.; Ma, J. "Electric Field Effects in Electro-optic Polyimides" presented at Wright-Patterson Air Force Base, Dayton, OH, February 1996.

14. *Lackritz, H. S.; Ostrowski, M. H. "Electric Field Effects in Polymer Thin Films for Second Order Nonlinear Optical Applications" presented at Antec 96, Society of Plastics Engineers, Indianapolis, IN, May 1996.

i * Number of submitted presentations: <u>10</u>

1. *Sullivan, L. A.; Lackritz, H. S. "Dynamic Mechanical Analysis and Dielectric Relaxation for Electro-Optical Polymer Applications" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

2. *Chen, F.; Subrahmanyan, S.; Lackritz, H. S. "Gas Phase Photopolymerization of Vinyl Monomers on Metallic Substrates Studied Using Surface Second Harmonic Generation" presented at the Materials Research Society national meeting in San Francisco, CA, April 1995.

3. *Ostrowski, M.H.; Lackritz, H.S. "Electric Field Effects in Poled Polymer Thin Films" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic Applications (at OSA national meeting) in Portland, OR, September 1995.

4. *Ghebremichael, F.; Lackritz, H.S. "Electro-optic and Second Harmonic Generation Studies of Dye-Doped Polymers" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic

5. Chen, F.; Subrahmanyan, S.; *Lackritz, H.S. "Studies of Photopolymerization at Metal Surfaces" presented at the American Chemical Society/Optical Society of America Symposium on Organic Films for Photonic Applications (at OSA national meeting) in Portland, OR, September 1995.

6. *Pasmore, T.A.; Talbot, J.; Lackritz, H.S. "Charge Transport through Polymer Thin Films for Second Order Nonlinear Optics" IEEE Conference on Electrical Insulation and Dielectric Phenomena, Virginia Beach, VA, October 1995.

7. *Ma, Z.; Lackritz, H. S.; Ermer, S.; Girton, D. G. "Thermal Stability Studies of DCM-Polyimide System for Second-Order Nonlinear Optical Applications" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

8. *Pasmore, T. A.; Talbot, J.; Lackritz, H. S. "Steady State Charge Transport through Molecularly Doped Polymer Thin Films for Second Order Nonlinear Optics" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

9. *Chen, F. C.; Lackritz, H.S. "Vapor Phase Photopolymerization of Acrolein on Metallic Substrates" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

10. *Ostrowski, M.H.; Lackritz, H.S. "Electric Field Effects in Poled Polymer Thin Film Systems" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

11. *Medvedev, G.; Caruthers, J.M.; Lackritz, H.S. "Theoretical Study of SHG Intensity Decay in Dye -Polymer Systems During Physical Aging" presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

12. *Zhuang, X.; Lackritz, H.S.; Shen, Y.R. "Photo-Isomerization of Polymer Monolayers and Multilayers on Water", presented at the American Physical Society national meeting in St. Louis, MO, March 1996.

j. * Honors/Awards/Prizes for contract/grant employees:

Effective August 1996: promotion to Associate Professor (with tenure); School of Chemical Engineering, Purdue University, West Lafayette, Indiana

June 1995   Visiting Professor, Chemical Engineering Consulting Group, E. I. DuPont Company Specialty Chemicals, Wilmington, Delaware

Presidential Faculty Fellows Award (National Science Foundation) 1993-1998

Office of Naval Research Young Investigator Award 1992-1995

Shreve Award for Outstanding Undergraduate Teaching, Second Place, Chemical Eng., 1994; 1995; 1996

American Chemical Society/Optical Society of America (ACS/OSA) Symposium on Organic Thin Films for Photonic Applications:
    International Advisory Committee 1994-
    ACS POLY Program Chair- 1995 Portland OSA meeting

Symposium Co-Chair- 1997 Long Beach OSA meeting
Symposium Co-Chair, Lead- 1998 Miami Beach ACS meeting

National Science Foundation Review Panels: NSF Graduate Fellowships, Directorate of Engineering, 1996

American Physical Society (Division of High Polymer Physics APS DHPP) Publications Committee (1993-) Publication Committee Chair, 1997
Guest Editor: Journal of Polymer Science: Polymer Physics 1997 APS DHPP Special Issue

Session Chair - "Conjugated and Conducting Polymers," American Chemical Society Meeting, August 1995, Chicago, IL

Session Chair - "Polymer Relaxation Dynamics," American Physical Society Meeting, March 1996, St. Louis, MO.

Session Chair - Antec 96, Society of Plastics Engineers, May 1996, Indianapolis, IN.

Symposium Co-chair and Organizer - "Polymeric Thin Films and Interfaces: Processing and Orientation Effects," American Institute of Chemical Engineers Meeting, to be held November 1996, Chicago, IL.

Minority Retention Program Chair, School of Chemical Engineering (Fall 1994-)

k.   Total number of **Full-time equivalent** Graduate Students and Post-Doctoral associates supported during this period, under this R&T project number:

Graduate Students: 4
Post-Doctoral Associates: 2
including the number of,
Female Graduate Students: 2
Female Post-Doctoral Associates: 0
Minority* Graduate Students: 0
Minority* Post-Doctoral Associates: 1
Asian Graduate Students: 1
Asian Post-Doctoral Associates: 1

Students funded under this and the AASERT grant include:
Dr. Stacey Fu (graduated Ph.D. 8/95)
Ms. Leah Sullivan (graduated MS 8/95 AASERT)
Mr. Daniel Randall (will graduate 6/96 MS AASERT)
Mr. Seung-Jin Lee (will graduate 8/98 Ph.D.)
post-doctoral associates: 6 months Lee-Yin Liu (Asian), 6 months Fassil Ghebremichael (minority)

l.   * Other funding see attached.

PART II: SUMMARY OF PROGRESS

a) PI: Professor Hilary S. Lackritz
b) Phone: (317) 494-4065; (317) 494-0805 fax; e-mail:lackritz@ecn.purdue.edu
c) ONR Scientific Officer: Dr. Kenneth J. Wynne, Chemistry Division

d) DESCRIPTION OF PROJECT

The objective of this research is to investigate the effect of structural relaxation of a polymer matrix near and below T_g on the orientation of dispersed chromophores. The proposed physical mechanism behind the strong coupling between the rotary diffusion of the chromophores and behavior of polymer microenvironment is the dependence of chromophore friction coefficient on the local and instantaneous value of polymer specific volume. Specific volume relaxation is described in terms of the Caruthers-Starry stochastic model in which the non-homogeneous distribution of specific volume through the sample is taken into account. A theoretical model and computer simulation algorithm that has been developed will enable the prediction of long time behavior of the SHG active orientational function $<Cos^3\theta>$ for a range of thermal and electric field histories.

e) SIGNIFICANT RESULTS

This work is the first attempt to propose a physically significant explanation of observed nonexponential behavior of the thermal and temporal stability of the SHG signal near and below T_g. It has been found that a simple model with a constant chromophore rotary diffusion coefficient is not appropriate and the non-homogeneity of a sample should be taken into consideration. A set of stochastic equations representing rotational dynamic of chromophore in the presence of relaxing polymer environment and external electric field has been obtained. A numerical algorithm for the solution of a set of non-linear stochastic differential equations has been developed. In contrast to a simple fit to the phenomenological KWW equation which provides little information about the mechanism of decay, the fit of experimental results with this theory gives information about polymer density distribution and estimation of the chromophore rotary diffusion coefficient.

f) PLANS FOR THE FOLLOWING YEAR

Various thermal and poling histories including up- and down- temperature jumps with different heating and cooling rates, and different poling and equilibration times will be investigated both analytically and experimentally for second order NLO materials. The comparison of simulated and experimental dependencies for the SHG signal decay will allow to adjust model parameter in order to successfully predict long term behavior of the materials during physical aging. We will continue also to develop more accurate model of chromophore-polymer interactions. The effect of dilation of polymer microenvironment caused by chromophore rotation will be taken into account through the representation of polymer as a viscoelastic fluid. Since the rotary diffusivity is now coupled to the rate of chromophore rotation, which directly depends upon the strength of the applied field, the model will predict experimentally observed nonlinear dependence of the NLO response on the applied poling field.

g) Graduate Students Funded in Year 1: Dr. Stacey Fu (graduated Ph. D. 8/95) funded 3 months; Mr. Seung-Jin Lee (will graduate 8/98 Ph. D.) funded balance

Part III.
a. Introductory view-graph discussing research
b. Figure representing the highlight
c. Concluding view-graph
d. Paragraph of explanatory text

This work is the first attempt to propose a physically significant explanation of observed nonexponential behavior of the thermal and temporal stability of the SHG signal near and below T_g. Currently there is no single model built upon physically reasonable postulates which describes experimental data and possesses predictive capability, especially for the long term behavior. The goal of this research is to develop theoretical model explaining physical mechanism behind the observable nonexponential decay of the SHG signal and relating characteristics of the decay to the material parameters of the polymer. The key assumptions is that the rate of chromophore rotation is controlled by the local and instantaneous density in the polymer matrix surrounding the chromophore. As shown in Figure 1, only those chromophore located in regions of sufficient specific volume have freedom to rotate through the considerable angles. This mechanism implies that chromophores should wait for the time comparable to the characteristic time of polymer structural relaxation until the next density fluctuation occurs and makes next rotation possible. The resulting temporal behavior of the SHG signal obtained as an average over the large number of simulated trajectories for individual chromophores is presented in Figure 2. In the simulation the material parameters for the commercial glassy polymer polymethylmethacrylate (PMMA) have been used. Obtained results are in qualitative agreement with an experimental data. A set of stochastic equations representing rotational dynamic of chromophore in the presence of relaxing polymer environment and external electric field has been obtained. A numerical algorithm for the solution of a set of non-linear stochastic differential equations has been developed. In contrast to a simple fit to the phenomenological KWW equation which provides little information about the mechanism of decay, the fit of experimental results with this theory gives information about polymer density distribution and estimation of the chromophore rotary diffusion coefficient.

Structural Relaxation in Polymers for Second Order Nonlinear Optical Applications

Hilary S. Lackritz,
Chemical Engineering, Purdue University
Chemistry Division: Dr. Ronald DeMarco, Director
Dr. Kenneth J. Wynne, ONR Scientific Officer

Developed new theoretical approach to investigate and predict thermal and temporal stability of nonlinear optical (NLO) chromophores doped into polymer hosts as a function of processing.

Physical postulates:
- chromophore rotary diffusivity is controlled by local and instantaneous density in the polymer host
- glassy polymer below Tg is spatially heterogeneous

Understanding of how characteristics of polymer and thermal and poling history affect chromophore orientation relaxation allows better tailoring of materials properties.

Figure 1. Nonhomogeneous structure of polymer glass below Tg. Chromophore rotary diffusivity is controlled by local density of the polymer.
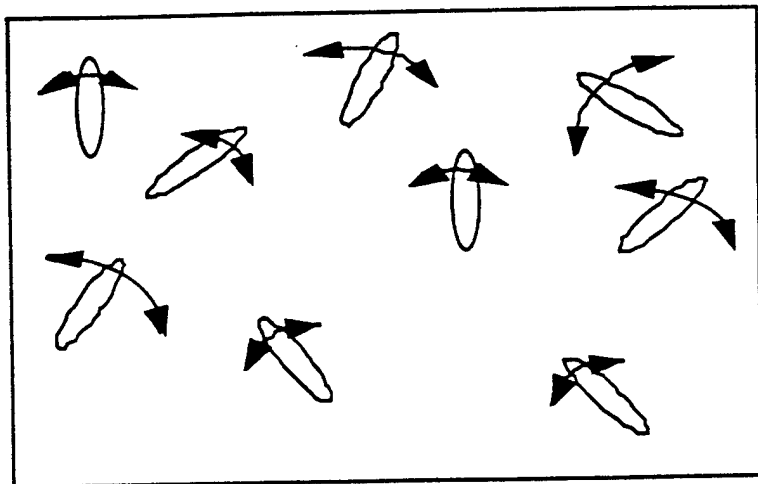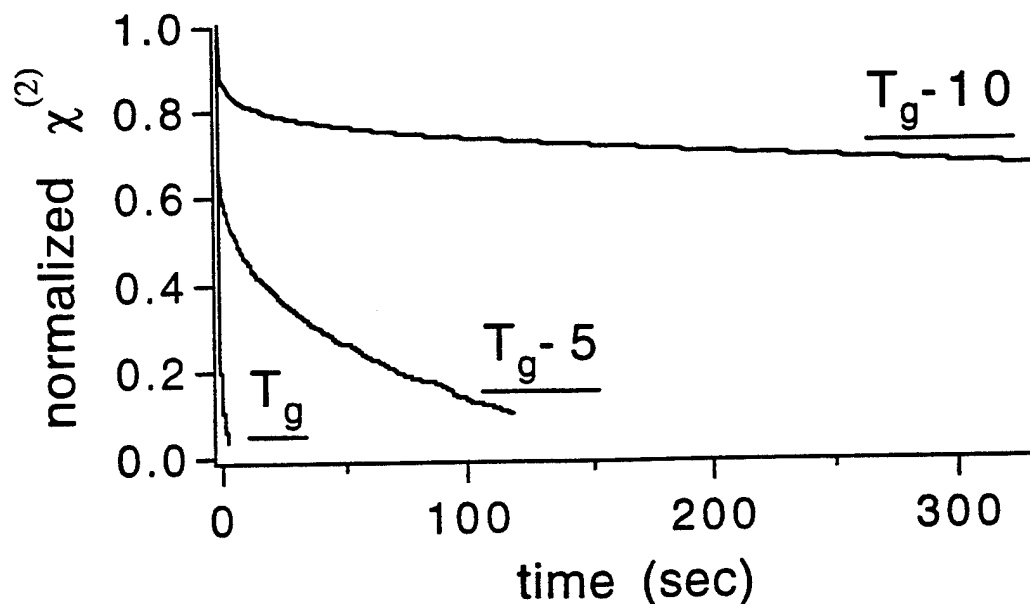

Figure 2. Simulated SHG response for PMMA doped with chromophores system at different temperatures.

Chromophore rotary diffusion coefficient $D=5\times10^6$ sec^{-1} at $T=Tg+20$.

Conclusions

Developed model for the orientational relaxation of NLO active chromophores dispersed into glassy polymer hosts that is able to qualitatively (at this time, and later quantitatively) reproduce experimentally observable nonexponential decay of SHG signal in these systems.

Important features of the model:
- based upon consequent thermodynamic theory of glassy state;
- based upon recent stochastic theory of structural relaxation which successfully predicts thermorheological complexity, nonlinearity and memory effects in glassy polymers;
- provides connection between chromophore rotary diffusivity and material properties of polymer matrix.

Novel theoretical approach promises to be predictive for cases of complex thermal and poling histories, which is important for preparation of materials for optical device application.

PART II: SUMMARY OF PROGRESS: AASERT GRANT No. N00014-93-1-0903

a) PI: Professor Hilary S. Lackritz
b) Phone: (317) 494-4065; (317) 494-0805 fax; e-mail: lackritz@ecn.purdue.edu
c) ONR Scientific Officer: Dr. Angela Erwin, Code 1113PO, Chemistry Division

d) Description of Progress

The method used to process a polymer ultimately determines the properties that polymer will exhibit. Processing conditions normally involve temperature changes that can influence the local mobility of the polymer as it relaxes toward equilibrium. The complex underlying polymer physics of this phenomenon is poorly understood. Our recent research focuses on studying how rapid changes in temperature affect the relaxation of volume near and below the glass transition region. Dilatometry, calorimetry, and other techniques used to study this type of phenomena measure bulk properties and take days to weeks to take measurements. It is our hypothesis that because second order nonlinear optics probes local motions in real time, it can sensitively measure small changes in the polymer microenvironment that can track local volume deviations.

e) SIGNIFICANT RESULTS

Systematic studies on how rapid temperature changes affect the relaxation of volume have been performed in guest-host NLO polymer systems. These studies include temperature jumps of varying magnitudes and directions, with NLO data shown to be reproducible and consistent with dilatometric and other data (which may take up to weeks to obtain). Phenomena such as rate dependencies, physical aging, and thermal and temporal stability may thus readily be studied. These experiments show the possibility of being sensitive enough to detect very small deviations in volume. A theoretical framework is being developed to relate this data to volume by making use of existing traditional models and more sophisticated models described in the parent funded project. In addition, other experimental methods such as dielectric relaxation and differential scanning calorimetry are being used to support the results that have been observed using this technique.

f) PLANS FOR THE FOLLOWING YEAR

This study will continue to explore the effect of temperature jumps, memory effects, autoacceleration, physical aging, and other phenomena on the relaxation of volume. The effect of more complex thermal histories, such as multiple temperature jumps (memory experiments) and actual manufacturing thermal treatments, will be investigated. The thermal history used during processing steps must be experimentally and theoretically understood before actual NLO devices will ever be commercially feasible on large scale.

g) Graduate student funded: Ms. Leah Sullivan (MS obtained 8/95), Mr. Daniel Randall (MS expected 8/96).

Part III.
a. Introductory view-graph discussing research
b. Figure representing highlight
c. Concluding view-graph
d. Paragraph of explanatory text

Processing conditions normally involve temperature changes that can drastically influence the local mobility of the polymer as it relaxes toward equilibrium. Most experimental and theoretical work to date has been on isothermal systems, or very simple temperature changes, and has been explained phenomenologically or not at all. It is therefore important to understand the underlying polymer physics that governs the relaxation following these rapid changes in temperature, and to experimentally and theoretically be able to explain, and hopefully predict, how the structural relaxation will affect overall material performance. This research attempts to monitor the volume and structural relaxation indirectly using second harmonic generation, a nonlinear optical process. This type of experiment is sensitive to the polymer microenvironment as relaxation occurs and thus is ideal for this type of study. The material studied in these experiments is poly(methyl methacrylate) (PMMA) doped with 2 wt.% 4 -dimethylamino-4'-nitrostilbene (DANS). In Figure 1, a typical decay curve of the second order susceptibility versus time is shown for a down temperature jump experiment. Figure 2 shows a typical result for the analogous up temperature jump of the same magnitude (but opposite direction) as that in Figure 1. Although these results are preliminary, they are being related to volume using a Narayanaswamy-type approach. These results are also being compared to thermodynamic based models and computer simulations done our research group. Other studies being performed include using dielectric relaxation to observe other modes of relaxation in order to get a better understanding of which parts of the polymer are responsible for which type of relaxation. Figure 3 shows a typical β transition for the same PMMA + 2 wt.% DANS material. The recent acquisition of a larger frequency and temperature range dielectric bridge (funded by Dow Chemical Company) will enable a more accurate study to be performed. All of these experiments help to understand the polymer physics that governs the relaxation process.

Structure Property Relationships and Polymer Physics in High Temperature Polymers for Second Order Nonlinear Optics.

VOLUME RELAXATION STUDIES FOLLOWING TEMPERATURE JUMPS USING SECOND HARMONIC GENERATION

Hilary S. Lackritz, School of Chemical Engineering, Purdue University

Chemistry Division; Dr. Ronald DeMarco, Director

Dr. Angela Erwin, ONR Scientific Officer

Polymer processing methods usually involve changes in temperature that influence the local mobility of the polymer as it undergoes volume relaxation

- Systematic studies on **how** changes in temperature affect the chromophore orientation in the polymer host

SPECIFIC ISSUES STUDIED:

- Comparison of temperature jumps of varying magnitudes and directions above and below the glass transition temperature and well into the glass.

- Establish connection between second order susceptibility measurements and volume relaxation

- Investigate how other modes of relaxation (dielectric, mechanical, etc.) affect the local polymer dynamics in these same materials
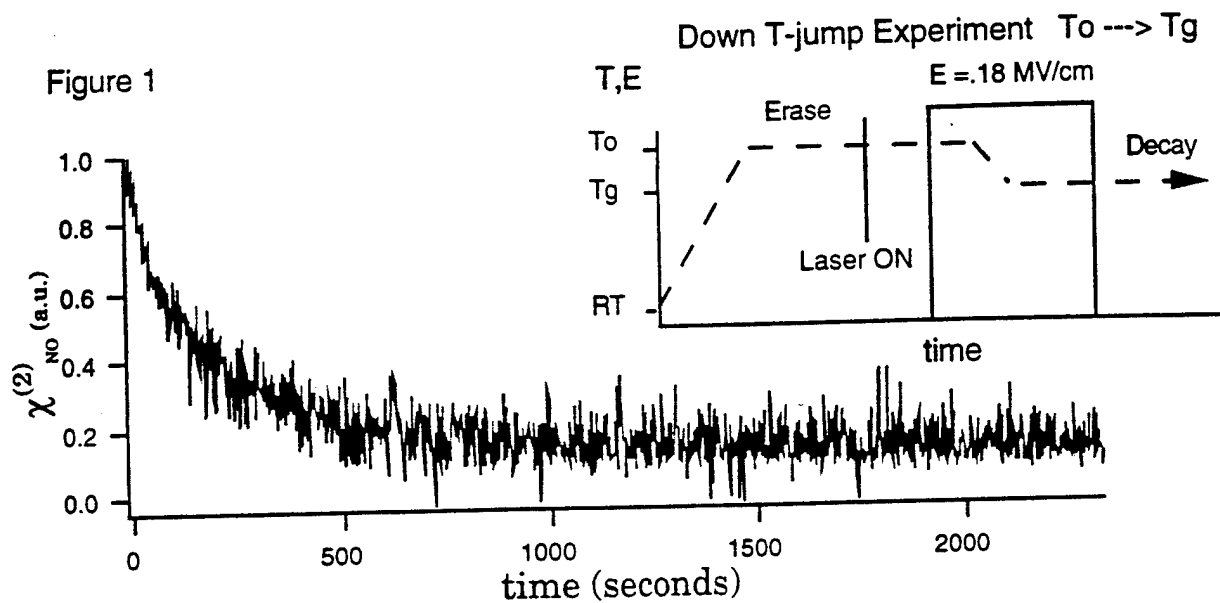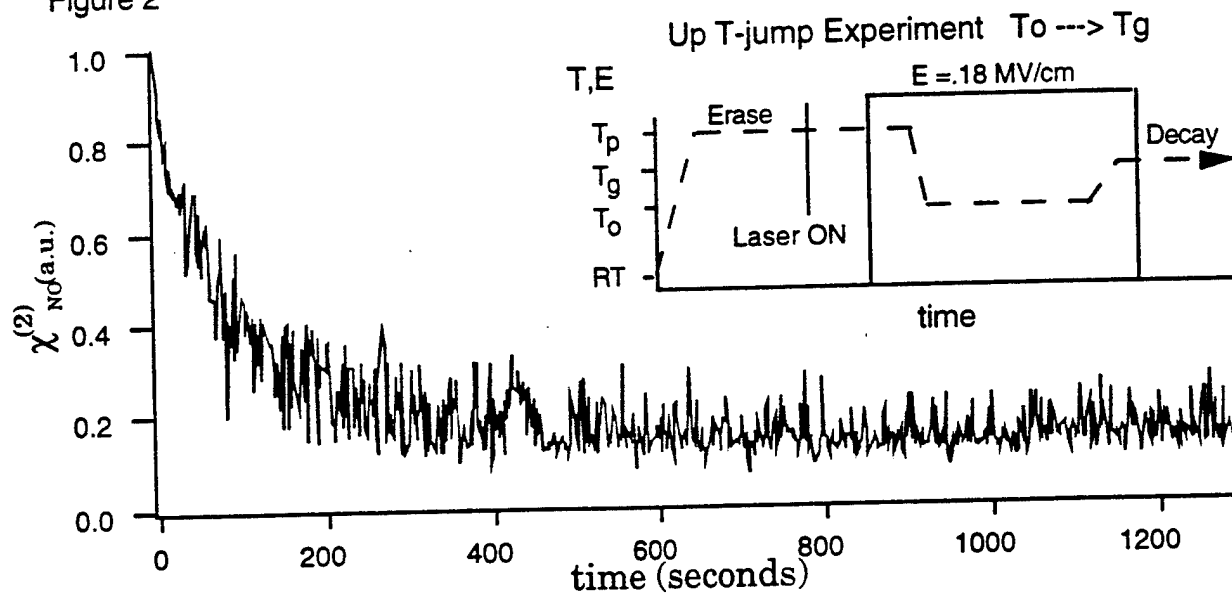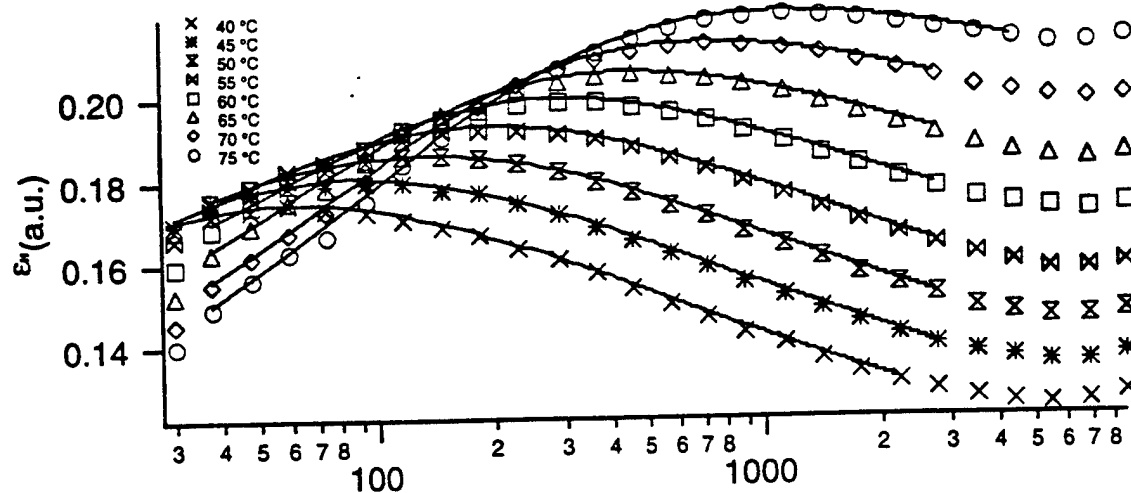
Figure 1

Figure 2

Figure 3

By understanding structural relaxation, can tailor materials/processing properties for improved device design

- Advantages of using nonlinear optical techniques:
  - sensitive to changes in polymer microenvironment
  - faster method (hours compared to days, weeks)
  - *in-situ*, real time measurements
  - can monitor current simultaneously

- Need to understand the complex underlying physics that accompanys volume relaxation

- Experiments will aid in the development of model that encompasses necessary thermodynamics instead of phenomenological fits

- Introduce multiple temperature jumps to examine the 'memory effects' shown by Kovacs et. al.- similar to the thermal processing undergone during commercial production.

By understanding the structure/property/processing relationship in NLO polymeric materials, can manufacture reliable, reproducible product with tailorable behavior.

Hopefully, can PREDICT how changes in thermal processing will affect thermal/temporal stability of these devices

PROJECT SUMMARY- LONG VERSION

The focus of this research is a critical study of the fundamental mechanisms for the generation and both the temporal and thermal stability of the nonlinear optical (NLO) properties of polymers doped with optically active chromophores. The experimental studies and models for describing relaxation in nonlinear optical materials to date have provided considerable insight; however, currently there is no single model built upon physically reasonable postulates as compared with empirical fitting that can unify the diversity in experimental data. Specifically, at temperatures well below T_g the chromophore reorientation after poling initially exhibits a relatively rapid reorientation which rapidly slows such that a net residual orientation persists for all experimentally accessible times. Assuming the rotary diffusion of the chromophore is controlled by the mobility of the matrix as indicated by the glassy polymer's mechanical and/or dielectric relaxation, the following difficulties arise: if the α-transition completely controls the relaxation process, why is chromophore disorientation observed so far below T_g and if the β-transition controls the relaxation process associated with chromophore disorientation (i) why does the residual orientation persist for times that much longer than the longest relaxation time for the b process and (ii) why is reorientation observed for polymers like polyindoles or polystyrene where the polymer matrix does not exhibit an observable mechanical or dielectric b-relaxation? Any physically realistic model for the NLO behavior of polymers must resolve this apparent disagreement between relaxation in the polymer matrix and relaxation of the chromophore reorientation, since all models implicitly assume that the relaxation of the matrix controls chromophore orientation. Any possibility for making extensions of any model to practical use conditions also requires this information. The objective here is to address this key question.

As a initial hypothesis we assume that (i) the rotary diffusivity is a function of the local temperature and specific volume and (ii) the local specific volume fluctuates around its mean. The key assumption is that the instantaneous rate of chromophore rotation is controlled by the *local* and *instantaneous* density and temperature in the polymer matrix surrounding the chromophore (rather than the spatial and temporal averages of these quantities). Initially we will assume that the chromophore rotation does not affect the local density and hence the rotary diffusivity. This assumption is valid if the matrix is modeled as an incompressible fluid; however, there will be some dilation upon chromophore rotation if the fluid is more accurately described as a slightly compressible viscous fluid. The second step will be to determine the local dilation as a function of the rate of the angular velocity for the rotation of a spheroidal particle in a slightly compressible Newtonian fluid, and if necessary this analysis will be extended to a slightly compressible linear viscoelastic fluid. The stochastic differential equation (SDE) for rotation of a single, spheroidal Brownian particle in the a viscous media with an applied external field will be formulated, where the resulting SDE is nonlinear because the rotary diffusion coefficient now depends upon the rate of angular rotation via the rotationally induced matrix dilation. The density fluctuations of the matrix will still have a significant affect on the rotary diffusion coefficient. Thus, the nonlinear rotational SDE will be solved simultaneously with the local volume SDE for a specific realization of chromophore rotation for the thermal and poling history under consideration; subsequently, the macroscopically observable NLO relaxation will be determined by averaging over an ensemble of realizations. Since the rotary diffusivity is now coupled to the rate of chromophore rotation which directly depends upon the strength of the applied external field, this model will naturally predict that nonlinear dependence of the NLO response on the applied poling field that has been observed experimentally.

We believe that the modeling perspective is consistent both with the existing experimental data and with the qualitative descriptions that have been used to rationalize that experimental data. The key assumption in the proposed approach as well as all previous models is that the chromophore rotation is controlled by the mechanical properties of the polymer matrix. the size and shape of the. and the torque induced by applied electric

material parameters in these relaxation models; rather, we will (i) independently measure the mechanical relaxation behavior of the polymer matrix and the relevant electrical behavior of the chromophores and matrix, (ii) predict the orientation and relaxation of the for various thermal and **poling histories**, and (iii) compare the predictions with experimental NLO data for the same thermal and poling histories. Thus, the **success of the proposed** research will require both accurate experimental determination of the necessary material behavior and careful implementation of the theoretical models described above.

ADDITIONAL INFORMATION: SELECTED ABSTRACTS OF MANUSCRIPTS TO BE PUBLISHED WITH OFFICE OF NAVAL RESEARCH GRANTEES

(note: I have submitted copies of each manuscript published with funds from this grant. Below I enclose abstracts of manuscripts in press, or submitted for your information. Note that these are manuscripts in which I am the "major" contributor; Professor Wright will be submitting his own version of this section.)

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Polymer Physics in Poled Polymers for Second-Order Nonlinear Optics

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ABSTRACT

A new class of high temperature stable polymers called poly(arylene ether) phosphine oxides is currently being investigated. These polymers are of interest for second-order nonlinear optical applications because of their high glass transition temperatures (>200°C). They also have strong hydrogen bonding sites that can interact with the chromophores. This work describes the polymer physics including structure/property relationships; in particular, the chromophore/polymer interactions and polymer backbone structures that influence the thermal and temporal stability of chromophore orientation in these polymer matrices. Second harmonic generation is sensitive to local changes in the polymer microenvironment, and thus is an excellent technique for probing chromophore orientational dynamics during and following electric field poling and the effect of dopant/polymer interactions on the temporal stability. Dielectric relaxation is employed to examine the intermolecular cooperativity and segmental relaxation behavior arising from different polymer backbone structures and steric effects. It is critical to understand how structure/property relationships affect the chromophore orientational dynamics and polymer relaxation in these polymers so that one can better tailor the materials for nonlinear optical device applications.

POLYMER PHYSICS AND STRUCTURE/PROPERTY RELATIONSHIPS OF THERMALLY STABLE POLYARYLENE ETHERS FOR SECOND ORDER NONLINEAR OPTICS

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ABSTRACT: This paper describes the structure/property relationships including the polymer backbone structures and molecular weight, chromophore/polymer interactions, and chromophore functionalization that influence the chromophore orientational dynamics and polymer relaxations in a special class of thermally stable polymers that was recently developed for second order nonlinear optical applications. These polyarylene ether polymers (synthesis and characterization reported elsewhere) are being investigated

randomization of chromophore orientation following electric field poling. They also have hydrogen bonding sites that can interact with the chromophores, which may improve the temporal stability of chromophore orientation following poling. Second harmonic generation, a second order nonlinear optical effect, and dielectric relaxation are the two techniques employed to examine the intermolecular cooperativity and segmental relaxation behavior in these polymers. By examining the second order nonlinear optical properties of the doped or functionalized polymeric material as a function of time and temperature, and the dielectric relaxation phenomena as a function of frequency and temperature, information concerning the local mobility and relaxation phenomena of the polymer microenvironment surrounding the nonlinear optical chromophores can be obtained. The dielectric loss data were analyzed using the Havriliak-Negami empirical function and the Schonhals and Schlosser model to examine the extent of intermolecular coupling in these polymer systems. Results obtained using these two techniques are correlated.

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ABSTRACT
Dielectric relaxation and second harmonic generation, a second order nonlinear optical technique, can be used to study the rotational Brownian dynamics of the nonlinear optical chromophores doped or functionalized into a polymer matrix as a function of time/frequency and temperature. By combining these two techniques, one can determine more quantitatively how the thermal and temporal stability of chromophore orientation relates to specific polymer motions. Furthermore, the relationships between the intra- and intermolecular cooperativity and polymer structures and properties can be better understood. This information is critical for designing novel nonlinear optical polymeric materials for optical device applications.

Study of Poling and Relaxation in Kink and Linear Main-Chain Functionalized Polymers for Second Order Nonlinear Optical Applications

ABSTRACT. The rotational dynamics of nonlinear optical chromophores functionalized to polymer main chains were studied using second harmonic generation. Corona poling was used to orient the chromophores into the bulk noncentrosymmetric structure required to observe second order nonlinearity. In order to detect different microscopic relaxation mechanisms of the polymers, chromophores were incorporated into the polymer main chain but positioned in two different ways. It was found that for a kink polymer, in which the chromophores were placed at an angle away from the major molecular axis of the polymer chain, the motion of the tilted chromophores may occur through local segmental motion. For a linear polymer, which had the same chromophore, but directed parallel to the chain direction, a large scale main-chain motion was involved in orientation. Therefore, the end-to-end vectors of the polymer chains could be detected. The temperature dependence of the second order nonlinearity in these polymers showed that there was an optimum temperature at which the main-chain chromophores could be relatively easily oriented during poling. The retarded polymer mobility at lower temperatures and the enhanced rotational Brownian motion at higher temperatures reduced the degree of the chromophore alignment and therefore a less second order signal was observed during poling. Dielectric relaxation spectroscopy showed that the bulk conductivity and crystallinity might also contribute to the decrease in second order nonlinearity observed at high temperatures.